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DTU Environment
Department of Environmental Engineering

PhD Thesis
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PREFACE

The work presented in this PhD thesis was carried out at the Technical University of Denmark at Department of Environmental Engineering under supervision of Philip John Binning (primary supervisor) and Poul Løgstrup Bjerg (co-supervisor). The work was conducted from July 2008 to April 2012. The PhD was carried out as a part of the project Innovative REMediation and assessment TEChnologies for contaminated soil and groundwater (REMTEC) and was primarily funded by the Strategic Research Committee and the Technical University of Denmark. The PhD thesis is based on six scientific journal papers, of which three are published. In the synopsis these papers are referred to by author names and Roman numerals (e.g., Chambon et al., I).

I. Chambon J.C., Binning, P.J., Jørgensen, P.R., and Bjerg, P.L., 2011. A risk assessment tool for contaminated sites in low-permeability fractured media. Journal of Contaminant Hydrology. 124 (1-4), 82-98.

II. Chambon, J.C., Bjerg, P.L., Scheutz, C., Bælum, J., Jakobsen, R. and Binning, P.J., 2012. Review of reactive kinetic models describing reductive dechlorination of chlorinated ethenes in soil and groundwater. Manuscript.

III. Bælum, J., Chambon, J.C., Scheutz, C., Binning, P.J., Laier, T., Bjerg, P.L. and Jacobsen, C.S., 2012. A conceptual model linking functional gene expression and reductive dechlorination rates of chlorinated ethenes in clayey groundwater sediment. Manuscript.

IV. Chambon, J.C., Broholm, M.M., Binning, P.J., and Bjerg, P.L., 2010. Modeling multi-component transport and enhanced anaerobic dechlorination processes in a single fracture - clay matrix system. Journal of Contaminant Hydrology. 112 (1-4), 77-90.

V. Manoli, G., Chambon, J.C., Bjerg, P.L., Scheutz, C., Binning, P.J., and Broholm, M.M., 2011. A Remediation Performance Model for Enhanced Metabolic Reductive Dechlorination of Chloroethenes in Fractured Clay Till. Journal of Contaminant Hydrology. 131 (1-4), 64-78.

VI. Chambon, J.C., Damgaard, I., Jeannottat, S., Hunkeler, D., Broholm, M.M., Binning, P.J., and Bjerg, P.L., 2012. Identification and localization of degradation processes in clay till by combined analysis of chemical and isotope data with a numerical model. Manuscript.

The papers are not included in this web-version, but can be obtained from the library at DTU Environment.

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Thanks to my colleagues from DTU Environment, and especially to the Butter Club, the Friday Bar, the Slackline Amateurs, the Monday Beer, the Scrabble Associates, the Bodega Crawlers, the Fondue Crew, the Coffee Break Regulars, the Brune Værthus' Venner, the EPA Members, the Cake Club, the Morning Swimmers and many others, for great fun, good company, and good excuses to relax. A big thanks goes to my office mates, Ida, Sanne and Timo for making such a cosy and nice atmosphere in and outside DTU. And I do not forget the "extended"-office mates Claire, Claus, Niels and Silvio. I will miss you!!!

A huge thanks to my friends outside the department for great support and lot of "non-PhD-related" fun!!! And finally to my family for their encouragement and their support.

SUMMARY

Chlorinated solvents are widespread contaminants in the subsurface. In low-permeability fractured media, such as clay tills, chlorinated solvents are transported downwards along preferential pathways, formed by fractures and sand lenses, and diffuse into the adjacent clay matrix. These contaminants are trapped in the low-permeability matrix and can then slowly back diffuse to the fracture network, forming a long-term secondary contamination source to the underlying aquifers. Because of the complex transport and degradation processes and the mass transfer limitations, risk assessment and remediation design are challenging. This thesis presents the development and application of analytical and numerical models to improve our understanding of transport and degradation processes in clay tills, which is crucial for assessing bioremediation performance and risk to groundwater. A set of modelling tools was developed, which includes analytical models for risk assessment, system of ordinary differential equations for reductive dechlorination, and numerical solutions for reactive transport in complex low-permeability fractured systems. Parameter estimation methods were used to calibrate and compare the model to various observations.

The risk assessment tools available do not take into account the complex transport processes occurring in clay tills, with fast breakthrough along preferential pathways, and long tailing because of slow back diffusion from the large storage capacity matrix. A risk assessment tool based on analytical solutions was developed and compared with existing approaches, and was shown to better reproduce trends observed in available data. However, the lack of long-term monitoring data prevents a thorough comparison of the conceptual models. Advanced numerical models for risk assessment are also required when complex processes, such as reductive dechlorination, are considered. For example, the formation of more mobile daughter products might increase the risk to the groundwater.

Reductive dechlorination is the major biotransformation pathway for chlorinated ethenes, and is a complex biological process where many bacterial populations interact. A thorough literature review has revealed that the processes controlling the growth of dechlorinating bacteria associated with dechlorination and the interaction of dechlorination with fermentation and redox processes are still uncertain. Therefore, the kinetic models developed to describe and predict reductive dechlorination have limited applicability, and a better understanding of

the microbial and geochemical processes is needed. For example, the expression of functional genes might be a better biomarker for ongoing reductive dechlorination than the number of dechlorinating bacteria. This is illustrated with the development of a conceptual model based on experimental data that links expression level of functional genes with dechlorination rates. The mathematical model was used to describe dechlorination dynamics in microcosm experiments.

Enhanced Reductive Dechlorination (ERD) has been suggested as a promising remediation technology for clay till sites, but knowledge of degradation processes in clay till and controlling processes is limited. The use of advanced numerical models has shown that it is necessary to overcome mass transfer limitations in order to achieve remediation in reasonable timeframes. The importance of mass transfer limitations depends on the extent of the reductive dechlorination in the matrix (termed bioactive zones), and the spacing between them, which is controlled by the injection interval.

Numerical modelling was applied to two ERD sites where discrete core sampling was performed in the source zone after injection of donor and bacteria. At Sortebrovej, modelling supported that bioactive zones were limited to narrow (5 cm) zones formed around high permeability features, which resulted in limited mass removal (< 20%) after 4 years. At Gl. Kongevej, reductive dechlorination was shown to be heterogeneous in the source zone, with an uneven distribution of bioactive zones. Modelling of mass removal in the source zone revealed that remediation timeframes vary between 20 and more than 50 years, depending on the distribution of biomass. The factors controlling the development of such bioactive zones in low-permeability media are still uncertain; and have been further investigated at a site where natural degradation has occurred for decades. The degradation processes have been identified and localized by employing an integrated approach combining chemical and compound specific isotope analysis of core samples, with reactive transport modelling. Biotic and abiotic degradation of chlorinated ethenes was documented in several zones inside the clay matrix, providing valuable knowledge which can be used to aid in the design of future remediation of chlorinated ethenes in low-permeability settings.

In conclusion, this PhD-project has developed our understanding on transport and degradation processes of chlorinated solvents in clay tills, and this knowledge was used to develop modelling tools for assessment of risk to groundwater and bioremediation performance in low-permeability media.

DANSK SAMMENFATNING

Chlorerede opløsningsmidler er en meget udbredt forureningstype i jord og grundvand. I lavpermeable aflejringer, eksempelvis moræneler, vil chlorerede opløsningsmidler især spredes via sprækker og sandlinser og derfra diffundere ind i den omgivende lermatrix. Forureningen er dermed fanget i den lavpermeable matrix og kan derfra langsomt diffundere tilbage til sprækkesystemet, hvilket skaber en langvarig sekundær kilde til forurening af de underliggende grundvandsmagasiner. De komplekse transport- og nedbrydningsprocesser samt diffusionsbegrænsninger medfører, at både risikovurdering og design af oprensning er en udfordring. Denne afhandling præsenterer udviklingen og anvendelsen af analytiske og numeriske modeller til at forbedre vores forståelse af transport- og nedbrydningsprocesser i moræneler, hvilket er afgørende for at kunne vurdere oprensningseffektivitet og risici for grundvand i forbindelse med biologisk oprensning. Der er udviklet et sæt af modelværktøjer, hvilket inkluderer analytiske modeller til risikovurdering, et system af ordinære differentialligninger til reduktiv dechlorering, og numeriske løsninger for reaktiv transport i komplekse lavpermeable opsprækkede systemer. Metoder til parameterestimation er anvendt til kalibrering af modellerne samt til sammenligning med data fra observationer.

Eksisterende risikovurderingsværktøjer tager ikke højde for de komplekse transportprocesser i moræneler med hurtigt gennembrud langs præferentielle strømningsveje og en lang udvaskningstid grundet den langsomme tilbagediffusion fra lermatricen. Et risikovurderingsværktøj baseret på analytiske løsninger er udviklet og sammenlignet med eksisterende metoder, og viste sig at være bedre til at gengive de tendenser, der ses i tilgængelige data. Der er dog en mangel på lange tidsserier, som betyder, at en direkte sammenligning af de konceptuelle modeller ikke kan foretages. Avancerede numeriske modeller til risikovurdering er også nødvendige når der skal tages højde for komplekse processer såsom reduktiv dechlorering. Eksempelvis kan dannelsen af mere mobile nedbrydningsprodukter medføre forøget risiko for grundvandsforurening.

Reduktiv dechlorering er den vigtigste biologiske nedbrydningsvej for chlorerede ethener og det er en kompleks biologisk proces, hvor mange bakteriepopulationer interagerer. Et omfattende litteraturstudium har vist, at de processer, der kontrollerer væksten af de dechlorerende bakterier, samt interaktionen mellem dechlorering, fermentering og redox-processer stadig er usikre. De kinetiske modeller, der er udviklet til at beskrive og forudsige reduktiv dechlorering, har derfor begrænset anvendelighed, og en bedre forståelse for de mikrobielle og geokemiske processer er nødvendig. Muligvis vil det være bedre som biomarkør for igangværende reduktiv dechlorering at anvende, hvordan de funktionelle gener udtrykkes, end at anvende antallet af dechlorerende bakterier. Dette er illustreret ved udviklingen af en konceptuel model baseret på eksperimentelle data, der sammenkæder, hvordan de funktionelle gener udtrykkes med dechloreringsrater. Den matematiske model er anvendt til at beskrive dechloreringsdynamikken i laboratorieforsøg.

Stimuleret Reduktiv Dechlorering (SRD) er blevet foreslået som en lovende afværgeteknologi for morænelerslokaliteter, men viden om nedbrydningsprocesser og betydende processer i moræneler er begrænset. Ved brug af avancerede numeriske modeller er det vist, at det er nødvendigt at overvinde diffusionsbegrænsningerne for at opnå oprensning indenfor rimelige tidshorisonter. Betydningen af diffusionsbegrænsningerne afhænger af udbredelsen af reduktiv dechlorering i matricen (benævnt bioaktive zoner), samt af distancen mellem dem, hvilket afhænger af injektionsintervallet.

Numerisk modellering er anvendt på to lokaliteter, hvor intakte kerneprøver blev udtaget i kildeområdet efter SRD. På Sortebrovej understøttede modelleringen, at de bioaktive zoner var begrænset til smalle (5 cm) zoner dannet omkring højpermeable indslag, hvilket resulterede i en begrænset massefjernelse (<20%) efter 4 år. På Gl. Kongevej viste den reduktive dechlorering sig at være meget heterogen med en uensartet fordeling af bioaktive zoner. Modelleringen af massefjernelsen i kildeområdet viste, at oprensningstiden varierer mellem 20 og mere end 50 år afhængig af fordelingen af de bioaktive zoner. Forståelsen for de styrende faktorer for udviklingen af sådanne bioaktive zoner i lavpermeable medier er stadig begrænset. Processer er blevet yderligere undersøgt ved hjælp af en kombineret anvendelse af kemiske analyser, stabile isotop analyser og reaktiv stoftransportmodellering på en lokalitet, hvor nedbrydning har foregået i årtier. Både biotisk og abiotisk nedbrydning blev påvist i zoner inde i lermatricen.

Samlet set har dette Ph.d.-arbejde bidraget til en forbedret forståelse for transport- og nedbrydningsprocesser for chlorerede opløsningsmidler, som er anvendt til at udvikle modelleringsværktøjer til risikovurdering over for grundvand og effektiviteten af biologisk oprensning i lavpermeable aflejringer.

LIST OF CONTENTS

1 INTRODUCTION

1.1 BACKGROUND AND MOTIVATION

Chlorinated solvents are widespread subsurface contaminants and one of the major threats for groundwater quality worldwide (Haggblom and Bossert, 2004). They are sparingly soluble dense non-aqueous phase liquids (DNAPLs) and can therefore migrate downward in the subsurface and be long term sources of contamination in groundwater, resulting from slow dissolution (McCarty, 2010). Furthermore because of their relatively high volatility (Staudinger and Roberts, 2001) they can also be a threat to indoor air quality.

Many contaminated sites in North America and Northern Europe occur in areas with low-permeability deposits, such as glacial clay tills, at the land surface (Christiansen et al., 2008; US EPA, 1994). These glacial clay tills are characterized by a high heterogeneity, with embedded high permeability features, such as fractures and sand lenses, in a low-permeability clay matrix (e.g., Kessler, 2012; Klint and Gravesen, 1999). At such sites, the released DNAPLs penetrate into preferential flow pathways formed by fractures and can then rapidly dissolve and diffuse from the fractures into the matrix (Falta, 2005; Lipson et al., 2005). Even after the removal of the physical source from the site, the contaminant trapped in the low-permeability matrix can diffuse back to the fracture network for hundreds of years, forming a long-term, secondary contamination source for underlying aquifers (e.g., Falta, 2005; Harrison et al., 1992; Parker et al., 1997).

Risk assessment at these contaminated sites is challenging because of the complex transport processes associated with such heterogeneous geology; fast downward movement of contaminants along preferential pathways (vertical fractures) and large storage capacity of the porous matrix. Furthermore such sites are challenging to remediate because of mass transfer limitations caused by slow diffusion processes in the low-permeability matrix (Christiansen et al., 2010; Johnson et al., 1989). Biological Enhanced Reductive Dechlorination (ERD), which has been successfully applied to sandy aquifers (e.g., Major et al., 2002; Scheutz et al., 2008), is a promising technology for *in-situ* remediation of chlorinated solvents at clay till sites. However current knowledge on controlling parameters for transport and degradation processes in clay tills is limited and therefore risk to groundwater and remediation timeframes are difficult to estimate (Damgaard, 2012; Freeze and McWhorter, 1997)

1.2 RESEARCH OBJECTIVES

The aim of this PhD study has been to improve our understanding of transport and degradation of chlorinated solvents in clay tills by integrated use of observations and reactive transport models and to use that understanding to develop analytical and numerical modelling tools for risk assessment and remediation design. The specific objectives of the project have been to:

- Develop a risk assessment tool for contaminated sites in fractured clay tills and compare it with existing approaches (Chambon et al. I)
- Review and assess the modelling approaches describing reductive dechlorination of chlorinated ethenes in soil and groundwater and evaluate the possibility of improving these models with new microbial techniques (Chambon et al. II; Bælum et al. III).
- Improved process understanding and identification of the controlling processes of enhanced and natural degradation of chlorinated ethenes in clay tills by integrated use of field observations, analytical chemical analyses, microbial analyses and advanced reactive transport models (Chambon et al. VI; Manoli et al. V).
- Identify the controlling parameters for remediation in clay tills using ERD and assess remediation timeframes by numerical models (Chambon et al. IV; Manoli et al. V)

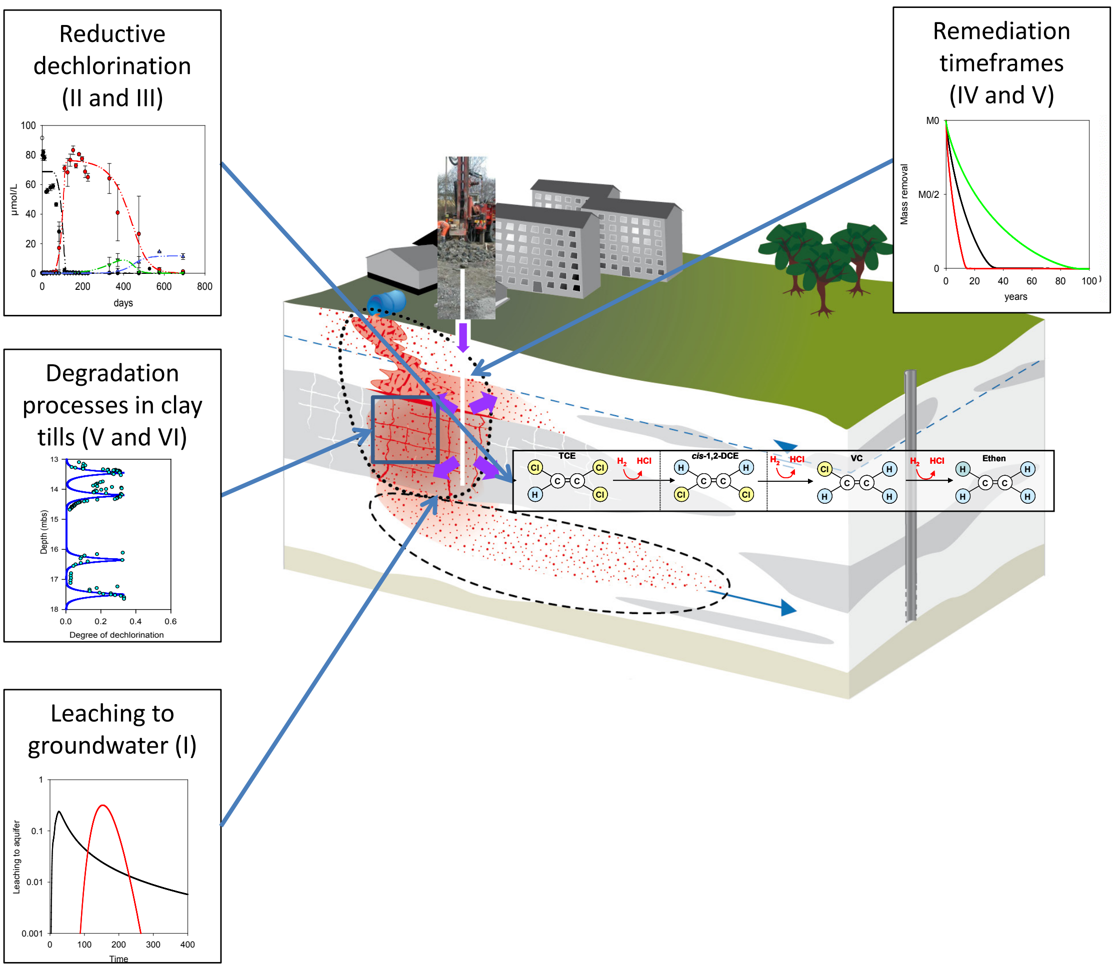

Figure 1. Overview of the thesis' objectives and papers at a clay till site contaminated with chlorinated solvents. The roman numeral of the relevant paper is indicated in brackets for each topic. Modified from Lemming (2010).

1.3 Outline of the PhD Thesis

The thesis focuses on the development of modelling tools for risk assessment and remediation design in clay tills. These tools are based on the findings and improved process understanding on the different aspects of transport and degradation of chlorinated solvents in low-permeability media, which are presented in the papers.

The analytical and numerical risk assessment tools are presented in Chapter 2, and the tools for assessing timeframes for bioremediation in clay tills are described in Chapter 3. The conclusions and suggestions for future research within the area are made in Chapter 4. The main content of the thesis is six scientific papers, which can be found in the appendices. Chapters 2-5 provide an overall frame for the papers and an overview of modelling tools for risk assessment and remediation design.

2 ANALYTICAL AND NUMERICAL TOOLS FOR RISK ASSESSMENT

Low-permeability fractured media are common in Northern Europe and North America (Christiansen, 2010; Klint and Gravesen, 1999; McKay and Fredericia, 1995) and are important to consider when assessing risk to groundwater at contaminated sites, because of the potential for fast downward movement of contaminants along preferential pathways (vertical fractures) and associated diffusion into the porous matrix. Contaminant transport to an underlying aquifer through such media is controlled by complex processes, resulting in potential fast breakthrough along fractures and large storage capacity in the porous matrix (Chambon et al., I). In such systems, most of the contaminant mass is trapped in the low permeability matrix as dissolved and sorbed phases (Falta, 2005; Freeze and McWhorter, 1997; Parker et al., 2010), forming a secondary contamination source, which results in long-term leaching to the underlying aquifer (Chambon et al., IV; Parker et al., 2008).

The need for risk assessment tools for groundwater has lead to research on tools which are suitable for the assessment of contaminant transport and risk in low permeability fractured media. Such risk assessment tools are also needed to determine clean-up criteria when performing remediation at contaminated sites (Danish EPA, 2011; Rodriguez and Kueper, 2012). Risk assessment is a trade-off between data availability, conceptual model complexity and result accuracy, and risk assessment in fractured clay till is particularly challenging because of its extreme heterogeneity

Risk assessment tools for chlorinated ethenes must address the additional complexity of having to deal with a sequential degradation chain including toxic metabolites such as vinyl chloride (VC). VC might be more mobile in low-permeability media than the parent compounds, resulting in enhanced contaminant mass flux of more toxic contaminants to the aquifer (Chambon et al., IV; Damgaard et al., 2012). In this chapter an overview of the existing tools for characterizing transport and leaching of contaminants in low-permeability fractured media is provided in Table 1. The relevance and limitations of four specific risk assessment tools, based on analytical solutions, are then described. Finally the use of numerical modelling tools in a risk assessment context is discussed.

Table 1. Overview of existing tools for characterization of transport and leaching of contaminants in fractured media

Vertical transport	**Steady-state (S)** **Transient (T)**	**Output** Concentration (C) Mass flux (MF)	**Source** Continuous (C) Pulse (P) Uniform* (U)	**Degradation** First-Order (F) Sequential (S)	**Risk assessment tool**	**Application in fractured media**
None	S	C	C U		JAGG 1.5[1]	
Exponential	T	C	U	F	CatchRisk[2]	Lemming et al., 2010b
Equivalent Porous Media	S and T	C MF	C P U	F S	Biochlor[3] Bioscreen	Chambon et al., IV
Dual Porosity	S and T	C MF	C	F	Consim[4]	Tang et al., 2010
Γmodel	T	C MF	U	F	REMChlor[5] (source)	Falta, 2005
Discrete Fracture	S and T	C MF	C P U	F	DTU-V1D[6]	Chambon et al., I

[1](Danish EPA, 2002); [2](Troldborg et al., 2008); [3](US EPA, 2000); [4](UK Environment Agency, 2003); [5](US EPA, 2007); [6](DTU Environment, 2011)

*Uniform source = contaminant is trapped inside the low-permeability fractured media, assuming uniform concentration

2.1 RISK ASSESSMENT BASED ON ANALYTICAL SOLUTIONS

In risk assessment, where many contaminated sites have to be screened on the basis of sparse site specific data, tools based on analytical solutions are usually preferred because limited data and software knowledge are required (Troldborg, 2010). However this means that some of the complex processes occurring during transport through fractured clay tills have to be disregarded in order to fit the conceptual models used in such solutions, these limitations are highlighted here and the use of more complex numerical models is discussed in the next section. The tools are based on analytical solutions and are presented in an order of increasing complexity (more processes are included), with a corresponding increasing level of required knowledge (more data/parameters are required).

The contaminated sites in low-permeability fractured media are divided in two categories, depending on the location of the contamination source (Figure 2):

- Contamination source is located above the low-permeability media (Figure 2a)
- Contaminant is trapped in the low-permeability media (forming a secondary source, Figure 2b)

Some risk assessment tools can only describe one of the two cases shown in Figure 2 (see Table 1).

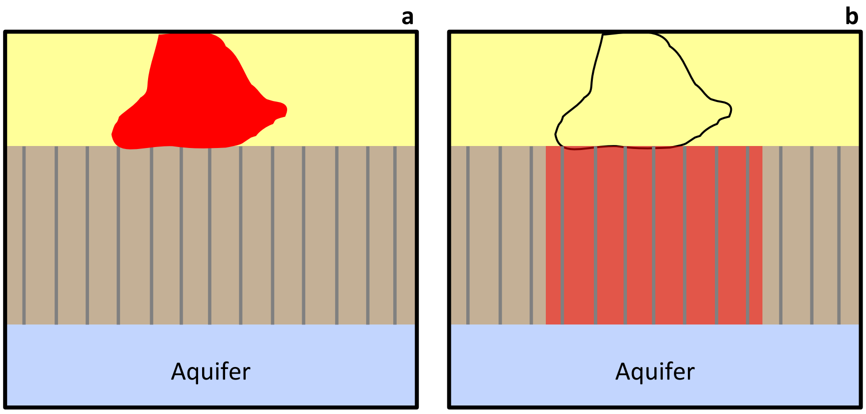

Figure 2. Conceptual sketch of the two source locations considered for risk assessment. a) Source above the fractured media. b) Contaminant trapped uniformly in the porous matrix (secondary source).

2.1.1 STEADY-STATE WITHOUT VERTICAL TRANSPORT (JAGG 1.5-TYPE)

This simple approach has been widely used for risk assessment and is not specific for transport in fractured clay tills, but has been applied to all types of geological media (JAGG 1.5, Danish EPA, 2002). The contaminant mass flux from a contaminant source is calculated based on the concentration measured in the source (C_0) and the net downward flow (corresponding to the net infiltration to the underlying aquifer (I) and the source area (A):

$$MF_{source} = C_0 \cdot I \cdot A \tag{2.1}$$

The resulting concentration in the underlying aquifer can then be calculated with a simple dilution model (C_1 and C_2 in Figure 3, JAGG 1.5). It can be seen that very little data is needed to compute risk assessment in this model (source concentration, net infiltration and source area), but neither vertical transport nor potential degradation are included. Furthermore the contaminant source is not described in this model, as the only site specific parameter is the net infiltration, source area and concentration.

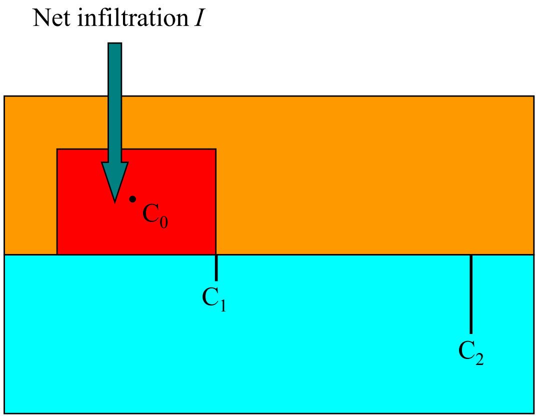

Figure 3. Conceptual model for risk assessment without vertical transport

2.1.2 Vertical transport based on Equivalent Porous Media (EPM)

In this approach vertical transport to the underlying aquifer is taken into account, and the fractured clay layer is represented by a homogeneous porous media with equivalent bulk hydraulic conductivity and porosity. The transport is one-dimensional, advection and dispersion are included and degradation can also be taken into account, and both steady-state and transient contaminant mass flux to the aquifer can be calculated. An analytical solution based on Van Genuchten and Alves (1982) is available for the two cases in Figure 2. Sequential degradation can also be taken into account, assuming the same retardation factors for all compounds (US EPA, 2000). Source concentration, equivalent hydraulic conductivity, equivalent porosity, net infiltration, longitudinal dispersivity and dispersion coefficient are needed to perform risk assessment based on the EPM. For low permeability media, advection becomes negligible and the vertical transport is controlled by molecular diffusion only. For fractured media, the presence of vertical fractures is implicitly taken into account by an increased hydraulic conductivity, a decreased porosity and longitudinal dispersivity (Chambon et al., I). The main limitation of this approach is that it is based on effective parameters (conductivity, porosity and dispersivity), that do not correspond to physical properties and cannot be measured. Therefore the model is of limited use for prediction because the parameters are expected to change from site to site, depending on flow physical scales and flow characteristics (Chambon et al., I).

2.1.3 Vertical leaching based on Γ model

This approach is based on a relationship between contaminant mass flux to the aquifer and mass removal in the source (e.g., Christ et al., 2006; DiFilippo and Brusseau, 2008; Falta, 2005):

$$\frac{C(t)}{C_0} = \left(\frac{M(t)}{M_0}\right)^{\Gamma} \tag{2.2}$$

where C_0 is the initial concentration discharging from the source, and M_0 is the initial contaminant mass in the source. The exponent Γ is an empirical parameter, which depends on source architecture and mass transfer processes. For the case of contaminant in low-permeability fractured media, the source zone corresponds to the contaminated clay till (Chambon et al., IV; Falta, 2005), as shown in Figure 2b. In such heterogeneous media, when most of the contaminant mass is located in low-permeability zones, the empirical exponent Γ tends to be greater than 1 (Falta et al., 2005; Falta, 2005). First-order degradation can be included, but the formation of daughter products and sequential degradation is not considered (Chambon et al., I). The main limitation of this approach is that it is based on an empirical exponent Γ, which varies from site to site, making its use for prediction limited.

2.1.4 Vertical transport in a Discrete Fracture (DF)

In this approach the presence of vertical fractures is explicitly taken into account, but the fracture network is simplified to a single fracture embedded in an infinite low permeability porous matrix. The transport through the fractured media is one-dimensional vertically along the fracture and one-dimensional horizontally in the porous matrix. The transport in the fracture is controlled by advection, while transport in the matrix is diffusion controlled (Chambon et al., IV).

Chambon et al. (I) derived an analytical solution based on the work of Tang et al. (1981), and both steady-state and transient contaminant mass flux can be calculated and first-order degradation can be included (though only uniformly in the fracture and matrix). Sequential degradation is not included, but analytical solutions exist if it can be assumed that transport parameters (retardation, diffusion) for all compounds are the same (Sun and Buscheck, 2003). Specific parameters for the description of the fractured media are needed for this approach (fracture spacing, aperture, and bulk hydraulic conductivity). Such parameters are often not available at specific sites, but can be derived from extensive field measurements performed in fractured clay tills Denmark (Jørgensen et al., 2004; Klint and Gravesen, 1999) and Northern America (McKay and Fredericia, 1995). In contrast to the EPM approach, this tool is based on geological physical parameters, and specifically models the physics of transport in fractured media; with fast breakthrough due to fractures and long tailings due to storage in the porous matrix. However this approach is also based on several simplifications of the real system (only vertical fully penetrating fractures, large fracture spacings, uniform degradation, no flow in the porous matrix, etc…). Therefore in a detailed site assessment, where more detailed processes are required (complex fracture networks, flow in the matrix, degradation in specific locations, sequential degradation, etc...), a numerical model might be necessary to overcome these limitations.

2.1.5 Illustration of the risk assessment tools

The output from the risk assessment tools described above are compared for the case of a typical fractured clay till for a conservative and a degradable compound for the two source configurations. It can be seen that they give very different results. The steady state model without vertical transport (the leaching concentration equal the source concentration) is obviously the most conservative, while the risk evaluated by the EPM and DF depends on the time at which it is considered. A more detailed comparison of EPM and DF tools can be found in Chambon et al. (I), while a comparison of DF and Γ models is presented in Chambon et al. (IV).

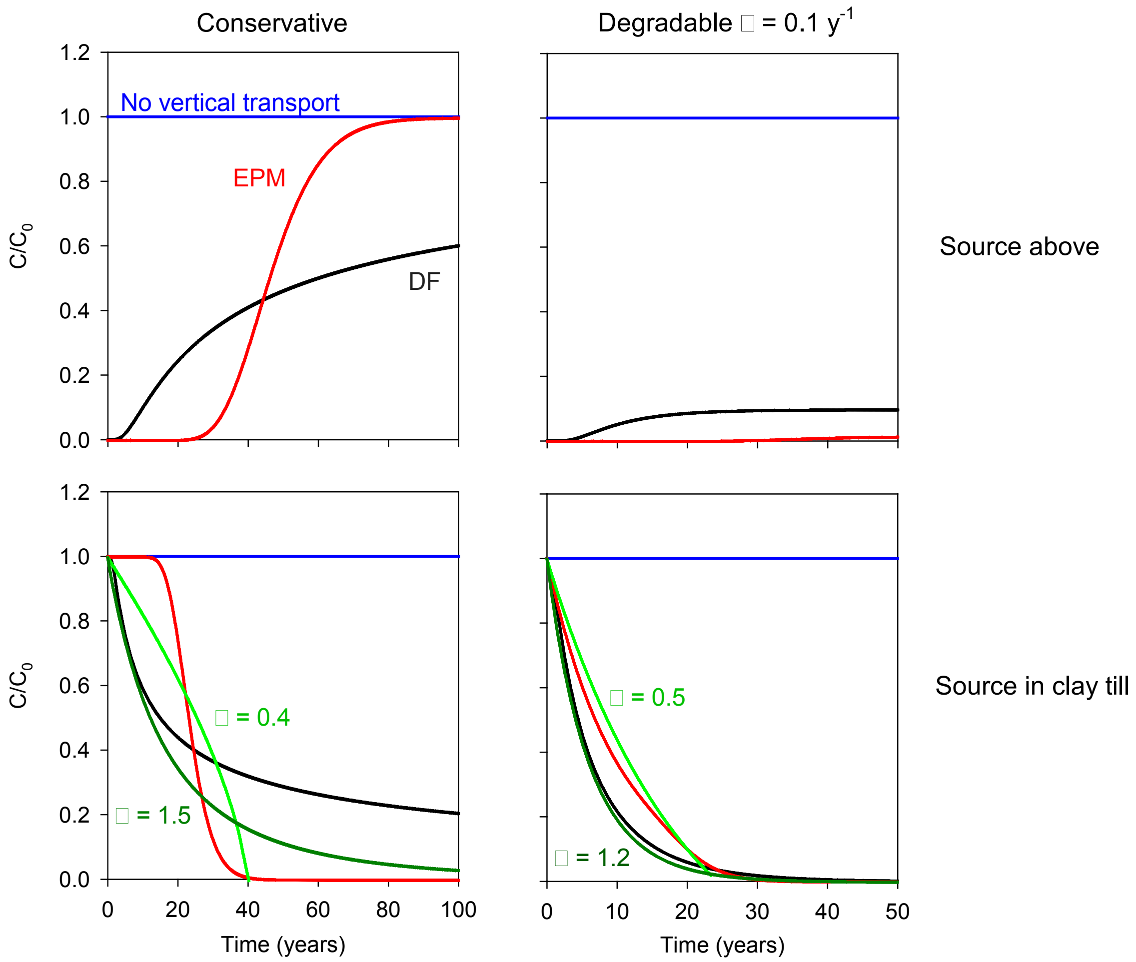

Figure 4. Illustration of the outputs of the four risk assessment tools described above, for the case of a conservative (left) and a degradable (right) compound. The top panels show results for a source above the clay till while the bottom panels show results for when the source is inside (bottom) the till.

2.2 Numerical modelling of heterogeneities in clay tills

When a detailed risk assessment is required, numerical modelling can be used to better take into account the role of the heterogeneities in the clay tills on contaminant transport, and thereby the risk to underlying aquifers. Such heterogeneities in clay tills include both vertical and horizontal fractures and sand lenses and stringers, which act as preferential pathways for flow and contaminant (Kessler, 2012). Many numerical models have been developed to simulate flow and transport in complex fracture networks (e.g., Molson and Frind, 2010; Slough et al., 1999; Sudicky and McLaren, 1992; Therrien and Sudicky, 1996). The main limitation of models which explicitly consider the fracture geometry is the limited site specific data usually available to accurately describe the heterogeneities in clay tills, for example the exact location of fractures at a site is almost never known. Therefore methods are needed to generate geological features with no or limited field data, such as stochastic fracture generators (e.g., Cacas et al., 1990; Graf and Therrien, 2007; Nordqvist et al., 1996), and multiple point statistics models for sand lenses (Kessler, 2012). Numerical modelling can then be used to assess the role of such heterogeneities and also the influence of their representations (stochastic, continuum, discrete) on contaminant transport and risk assessment.

Numerical modelling is also needed when simulating complex degradation models (e.g., Chambon et al. IV; Rotter et al., 2011), such as those describing reductive dechlorination, which is generally represented by Monod kinetic models including bacterial growth (Chambon et al. II). For sequential degradation, the fate of the daughter products is also important for risk assessment and can be assessed with numerical models employing compound-specific transport properties (such as diffusion and sorption coefficients). For example, numerical modelling is necessary to simulate the enhanced leaching of more mobile daughter compounds (cis-DCE and VC) originating from reductive dechlorination of their parent compounds in fractured clay till (Chambon et al. IV; Lemming et al., 2010a). Multiple degradation pathways (abiotic and biotic cis-DCE degradation, for example) can also occur concurrently in clay tills (Chambon et al., VI), in which case the use of numerical modelling to assess contaminant attenuation might be necessary.

2.3 MODEL VALIDITY AND OUTLOOK

A range of tools are available for risk assessment in fractured clay tills, as presented above. Given limited time and available data, risk assessment becomes a trade-off between model complexity and accuracy. It is very difficult to verify the accuracy of the developed tools, given the long timeframes for contaminant transport in such low-permeability media. There is a lack of long-term monitoring data in fractured clay tills and this makes it difficult to compare the models and choose the most accurate (Chambon et al., I; Fischer et al., 2010; Kohne et al., 2009; Tait et al., 2004). Because of this lack of long term data the controlling processes in such fractured media are still debated (Harrar et al., 2007; Helmke et al., 2005); is it advection along the fractures or diffusion in the clay matrix that controls the risk to an underlying aquifer? Numerical investigations using long-term monitoring data are necessary to develop practical tools which include the relevant processes with the right level of complexity.

3 TIMEFRAMES FOR BIOREMEDIATION IN CLAY TILLS

Remediation in low-permeability media, such as clay tills, is challenging because of mass transfer limitations, due to the slow diffusion transport processes in the matrix (Chambon et al., IV; Manoli et al. V). This leads to long cleanup timeframes, and is a major barrier for *in-situ* remediation technologies. In order to select appropriate remediation technologies and design of reliable remediation strategies it is therefore important to identify the controlling parameters and processes. A crucial parameter in remediation design is remediation timeframes and in this study they refer to both times for mass removal of contaminant in the low-permeability source and for contaminant mass flux reduction, corresponding to a risk reduction to the aquifer. In this chapter, literature examples of timeframe assessment for *in-situ* remediation are presented, then the controlling parameters are discussed, and finally an outlook on the use of practical tools for remediation design and possible improvements for remediation success in low-permeability media is given.

3.1 TIMEFRAME ASSESSMENT IN THE LITERATURE

Several examples of cleanup time assessment for chlorinated ethenes in low-permeability media (especially fractured clay and bedrock) are summarized in Table 2. The timeframes for contaminant mass removal by clean water flushing through the fracture networks vary between 420 and more than 1000 years, depending on the physical and hydraulic characteristics of the system (fracture aperture and spacing, hydraulic gradient), and the diffusion transport in the matrix (matrix porosity, sorption and diffusion coefficients). This shows that clay tills can act as a long-term secondary source with contaminant leaching to underlying aquifers over periods of hundreds of years (e.g., Chambon et al., IV; Seyedabbasi et al., 2012). These timeframes are reduced when first-order decay can be assumed in the matrix, due to natural attenuation (e.g., Falta, 2005; Rodriguez and Kueper, 2012).

Timeframes for remediation with In-Situ Chemical Oxidation (ISCO) and Enhanced Reductive Dechlorination (ERD) vary between 30 and 200 years, depending mainly on the degradation location in the matrix and the degradation rates, as discussed further in the next section. Several studies have also shown that if mass removal is incomplete in the source zone, concentration rebound up to pre-remediation level can be expected due to back diffusion (e.g., Freeze and McWhorter, 1997; Manoli et al., V; Mundle et al., 2007).

Table 2. Examples of timeframe assessment for remediation in low permeability fractured media

Reference (Field site)	Geology Contaminant	Remediation	Model (2D) for assessment	Timeframes in years	Controlling parameters
Freeze and McWhorter, 1997	Low permeability TCE	Four generic technologies	Qualitative	Months to decades Risk of rebound	
Reynolds and Kueper, 2002	Fractured clay PCE/TCE	Clean Water Flushing	Single fracture	500-1000	Sorption, Porosity Diffusion
Falta et al., 2005	Fractured clay TCE	Clean Water Flushing 1st order decay	Parallel fractures	>1000 150 (deg)	Fracture aperture Degradation rate
Lipson et al., 2005	Fractured bedrock TCE	Pump&Treat	Parallel fractures	>1000	Sorption, Porosity Diffusion
Mundle et al., 2007	Fractured clay PCE/TCE	ISCO†	Parallel fractures	5 (followed by rebound)	Sorption, Porosity Fracture spacing
Chambon et al., III	Fractured clay TCE	None ERD* (in 5cm zone along fracture and whole matrix)	Parallel fractures Monod kinetic Unlimited donor	419 (None) 32 – 195 (deg)	Degradation location & rate Fracture spacing Sorption, Porosity
Lemming et al., 2010a (Gl. Kongevej)	Fractured clay TCE	None ERD (in 10cm zones spaced 25cm)	Parallel fractures Monod kinetic Unlimited donor	1200 (None) 38 (ERD)	
Damgaard, 2012; Manoli et al., V (Sortebrovej)	Fractured clay TCE	ERD (in 5cm zones spaced ≈ 1m)	1D diffusion Monod kinetic	5 (18% mass) >50	
Rodriguez and Kueper, 2012	Fractured bedrock TCE	Clean Water Flushing 1st order decay	Parallel fractures	1 to 10,000	Thickness Spacing, Aperture, Porosity Degradation rate
Damgaard et al., 2012 (Gl. Kongevej)	Fractured clay TCE	ERD (variable degradation locations)	Parallel fractures Monod kinetic Unlimited donor	≈ 50	Degradation location
Lemming et al., 2012 (Sortebrovej)	Fractured clay TCE	None ISCO (in 10cm zones spaced 1m) ERD (in 5cm zones spaced 1m)	Fracture network Monod kinetic Unlimited donor	670 (None) 80 (ISCO) 90 – 200 (ERD)	Degradation rates

†ISCO = In-Situ Chemical Oxidation. *ERD = Enhanced Reductive Dechlorination.

3.2 CONTROLLING PARAMETERS FOR BIOREMEDIATION IN CLAY TILLS

Several factors control the efficiency of remediation in clay tills, and they are presented here in three categories; site specific parameters controlling flow and transport in the source zone, biogeochemical parameters controlling degradation processes, and design parameters, which depend on the remediation strategy. In this section, ERD of chlorinated ethenes is the primary focus of the discussion, but most of the issues are also relevant for other *in-situ* technologies, such as ISCO. The principles of ERD of chlorinated ethenes in clay tills are presented first.

3.2.1 ERD OF CHLORINATED ETHENES IN CLAY TILLS

The most important biotransformation pathways for PCE and TCE is reductive dechlorination, where PCE and TCE are sequentially dechlorinated to the metabolites dichloroethylene (DCE, mainly cis-DCE), vinyl chloride (VC) and finally ethene (Figure 5) (Chambon et al., II; Maymo-Gatell et al., 1997). This process requires anaerobic conditions, an electron donor (usually hydrogen), a carbon source (usually acetate), and specific degraders (Chambon et al., II). When enhanced dechlorination is employed in a remediation technology, natural degradation processes can be enhanced by injecting specific dechlorinating bacteria (bioaugmentation) and/or organic electron donors (biostimulation) into the subsurface. The injected organic donor (vegetable oil, lactate, molasses, etc.) is fermented to produce hydrogen that can be used by the bacteria for dechlorination. The produced hydrogen is also used by other geochemical processes, such as sulphate and iron reduction or methanogenesis. Many bacteria are known to dechlorinate PCE or TCE to cis-DCE (e.g., *Geobacter*, *Desulfitobacterium*), but only some bacteria of the genus *Dehalococcoides* (*Dhc*) can perform complete dechlorination to the non-toxic compound ethene (Chambon et al., II). Therefore the injection of a bacterial community, containing *Dhc*, is often required to ensure the complete dechlorination of chlorinated ethenes to ethene, and avoid accumulation of intermediate products (cis-DCE and VC) (Fennell et al., 2001; Major et al., 2002).

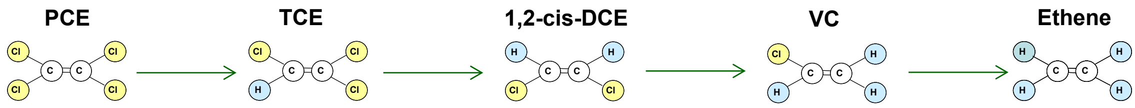

Figure 5. Sequential reductive dechlorination of PCE to ethene.

In low-permeability media, such as fractured clay till, the main challenge is to ensure contact between the contaminant trapped in the low-permeability matrix and the injected donor and bacteria (Christiansen, 2010; Damgaard, 2012). It is usually assumed that the amendments spread in horizontal high permeability features (induced or naturally occurring fractures and sand stringers), from which donor and bacteria can spread further into the adjacent matrix to form bioactive zones (Figure 6), where chlorinated ethenes are degraded (Damgaard, 2012; Manoli et al., V; Scheutz et al., 2010).

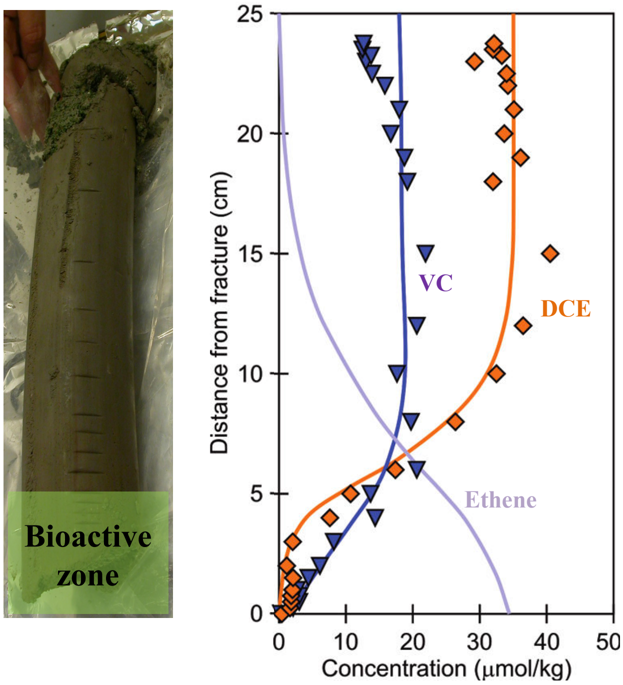

Figure 6. Illustration of the development of a bioactive zone in the matrix (modified with permission from Scheutz et al., 2010. Copyright 2012 American Chemical Society)

3.2.2 SITE SPECIFIC PARAMETERS

ERD in low-permeability media is subject to mass transfer limitations, due to slow diffusion transport processes in the matrix, and so the parameters controlling transport in the matrix greatly affect model predictions (Chambon et al., IV). These parameters are mainly porosity, tortuosity and sorption coefficients, and the diffusion coefficients, which are compound specific (Chambon et al., I). Tortuosity is usually assumed to be equal to the matrix porosity (Chambon et al., I and IV), but can vary significantly in clayey deposits and affect effective rate of diffusion (Parker et al., 1994; Parker et al., 2004). Sorption also affects effective rate of diffusion, and it is also relevant to assess contaminant mass stored in the source zone, and the effective rate of degradation occurring in the aqueous phase. Sorption of chlorinated ethenes has been shown to be higher than typically expected in clay tills (Lu et al., 2011), thus influencing the remediation timeframes significantly (Chambon et al., IV; Manoli et al., V).

The hydrogeological parameters controlling flow through fractured media (fracture spacing, aperture, bulk hydraulic conductivity, recharge) are important when most of the contaminant mass in the source zone is removed via leaching to the aquifer, and not as a result of effective remediation via ERD (Chambon et al., IV). These parameters also have a significant impact on the risk to the aquifer, as they control contaminant mass discharge from the source zone (DTU Environment and Orbicon, 2012).

Finally parameters related to the source characteristics, such as thickness of the contaminated clay till and initial contaminant concentration, affect remediation efficiency; decreasing the source thickness results in a flux reduction to the aquifer (DTU Environment and Orbicon, 2012), while a higher initial concentration can slow down reductive dechlorination due to inhibition (Chambon et al., II; DTU Environment and Orbicon, 2012).

3.2.3 Biogeochemical parameters

The parameters controlling degradation in clay tills influence both mass removal and contaminant flux to the aquifer. The extent of dechlorination in the clay till matrix, e.g. the thickness of the bioactive zone developing in the matrix adjacent to the injection depth, is crucial to assess remediation timeframes, and can vary significantly between sites and locations at the same site (Chambon et al., VI; Damgaard et al., 2012). A bioactive zone of 5cm on one side of a hydraulic fracture was reported 150 days after injection at the ERD pilot scale site (Rugårdsvej, Figure 6), while degradation products were measured more than 25 cm from the fracture 540 days after injection (Scheutz et al., 2010). At a full scale ERD site (Sortebrovej), modelling has shown that bioactive zones in the source zone were limited to 2.5 cm on each side of the naturally occurring sand stringers both 2 and 4 years after injection (Manoli et al., V), resulting in long expected timeframes (> 50 years) for remediation (Damgaard, 2012). Core sampling at another full scale ERD site (Gl. Kongevej) 4 years after injection showed very heterogeneous dechlorination, with bioactive zones varying between few centimetres around high permeability features to larger zones (up to 1.8 m), and remediation timeframes assessed by models vary from more than 50 to less than 20 years (Damgaard et al., 2012). The processes controlling the development of such bioactive zones are still uncertain, but recent investigations using discrete core sampling for analysis of concentration and isotope data combined with reactive transport modelling at a site, where natural attenuation has occurred for decades, have lead to improved process understanding (Chambon et al., VI).

Reductive dechlorination is usually modelled using Monod kinetics, and is then controlled by the kinetic parameters, such as the maximum growth rates and half velocity constants, and the concentration of specific degraders (Chambon et al., II). A wide range of kinetic parameter values have been reported in the literature, mainly based on laboratory batch experiments, and so predictions of reductive dechlorination rates are very uncertain when assessing remediation timeframes, which can vary significantly depending on the chosen rates (Lemming et al., 2012). Furthermore kinetic parameters also influence the production and degradation of daughter products, especially production and leaching of VC, which can result in increasing risk to the aquifer (Chambon et al., IV; Lemming et al., 2012). The production of VC is also dependent on the competitive inhibition model used in Monod kinetics and inhibition constants, which have been shown to vary significantly in the literature (Chambon et al. II).

The concentration of specific degraders, must also be specified in the models and can vary by several orders of magnitude between sites (Chambon et al., II), with reported values of 10^7-10^8 and 10^{10} *Dhc* copies/L after bioaugmentation in Scheutz et al. (2010) and Hood et al. (2008), respectively. This parameter also greatly influences mass removal efficiency, especially for wide bioactive zones; e.g., increasing the biomass concentration by one order of magnitude can decrease the cleanup time by 90% when degradation occurs in the whole system (Chambon et al., IV).

Remediation timeframes are mainly controlled by either diffusion or by reaction processes, depending on the thickness of the bioactive zones and the distance between them (see injection interval in section 3.2.4).

Other degradation processes can also influence fate of chlorinated ethenes in clay tills. For example, abiotic degradation of cis-DCE, has been shown to play an important role for natural attenuation (Chambon et al. VI; Darlington et al., 2008) and may be a relevant pathway for remediation.

3.2.4 Design parameters

Several technologies are available for the injection of reactants into low-permeability media and enhance delivery of *in-situ* remediation amendments (Christiansen et al., 2010). Mass transfer limitations and remediation timeframes, depend on the combination of injection interval and bioactive zone thickness (DTU Environment and Orbicon, 2012). The injection interval determines the spacing between amended fractures/stringers (assuming successful injection at each depth interval). A recent field study (Christiansen et al., 2010) has shown successful tracer amendment down to 9.5 mbs at 25 cm intervals using direct push delivery, and 1 meter intervals using pneumatic fracturing. Successful amendment with bacteria and electron donor was documented with 25 cm interval using direct push delivery in a full scale ERD application (Damgaard et al., 2012). Depending on the thickness of the bioactive zones in the matrix, closely spaced injection can ensure reductive dechlorination in the whole system (Christiansen et al., 2012). At a full scale ERD application in clay till (Sortebrovej), amendment with gravitational injection resulted in donor spreading in 5 cm reaction zones, with 1 meter vertical spacing, resulting in limited mass removal (less than 20% after 5 years, Manoli et al., V) and long remediation timeframes (> 50 years, Damgaard, 2012).

Most of the modelling studies of ERD have not considered donor limitations, and have assumed optimal conditions for reductive dechlorination (e.g., Chambon et al., IV; Lemming et al., 2010a; Torlapati et al., 2012). However donor consumption, by dechlorination and other competing processes, can result in the need for re-injection in the subsurface and is an important factor which must be considered in remediation design, influencing both remediation cost and environmental impacts (Lemming et al., 2010a; Semkiw and Barcelona, 2011). Some tools and methods are available to estimate donor consumption, depending on redox parameters but they cannot be used to assess lifetime in the subsurface and the need for re-injection (US Air Force, 2004; Robinson and Barry, 2009). In Manoli et al. (V), organic substrate fermentation and hydrogen consumption were included in a numerical model of ERD in clay till and predicted that the vegetable oil would be depleted 5 years after injection. Experience from other sites undergoing ERD in fractured clay tills have shown that similar timeframes are expected for donor lifetime, so that a 5 year injection frequency is needed (Damgaard, 2012). Short-term donor consumption depends mainly on competing electron acceptors (nitrate, sulphate,…), but long-term consumption is mostly influenced by methanogenesis, and potentially by iron reduction of stable iron oxides (Chambon et al., II).

3.3 OUTLOOK

The influence of the controlling parameters on remediation timeframes and efficiency of ERD in clay tills can be assessed by advanced numerical modelling, but the combination of complex processes make it difficult to develop simple practical models that can be used for screening purposes and remediation design at multiple sites. However it is possible to develop practical tools, that are based on multiple simulations of more complex models, which can then be presented in a user-friendly framework. DTU Environment and Orbicon (2012) developed such an Excel-based practical tool, which can assess mass removal and flux reduction for ERD in clay tills for multiple combinations of controlling parameters. These outputs can be used for optimization of remediation design, and also as input to other decision-making support tools such as life cycle assessment and environmental economic assessments to guide remedial choice (Lemming et al., 2010a; Lemming et al., 2012).

The accuracy of model assessments of remediation timeframes is difficult to assess, because of the limited amount of long term data available and the limited number of field scale ERD applications in clay tills (Damgaard, 2012). Model results depend on the way that the models describe the controlling processes, and are uncertain. For example reductive dechlorination is generally modelled by a Monod kinetic approach, in which the concentration of specific degraders controls the rate (Chambon et al., II). However recent studies suggest that this might not be the best indicator for ongoing microbial processes, and that the expression of functional genes (mRNA of e.g., *tceA*, *vcrA* or *bvcA*) might be the controlling parameters for dechlorination (Bælum et al., 2008; Bælum et al., III; Johnson et al., 2005; Koutinas et al., 2011). New microbial techniques may provide important new data that can improve process understanding, and future modelling efforts (Chambon et al., II). Finally the development of bioactive zones in the matrix, which is a crucial process for successful remediation using ERD, is still uncertain, and the parameters are not well known (Chambon et al. VI; Damgaard, 2012; Manoli et al. V).

4 CONCLUSIONS

The aim of this PhD study has been to improve our understanding of transport and degradation of chlorinated solvents in clay tills and to use that understanding to develop modelling tools for risk assessment and remediation design. Based on the thesis, including the six papers, the following key findings have been made:

- A literature review has revealed a lack of modelling tools for risk assessment in low-permeability fractured media, and so a tool was developed based on analytical solutions, that take into account complicating factors of transport through fractured media. Comparison of the developed tool with existing approaches such as the equivalent porous media model reveals significant discrepancies in the assessed risk.

- Reductive dechlorination is the major biotransformation pathway for chlorinated ethenes, but current modelling approaches are unable to adequately model the processes occurring, as revealed by a comprehensive literature review. The review shows that the link between bacterial growth, number of dechlorinating bacteria and dechlorination rates is not well described by Monod kinetics. The interaction between redox processes and reductive dechlorination is not well understood experimentally, and so existing metabolic models are deficient.

- A conceptual model linking the mRNA expression level of functional genes and dechlorination rates was developed based on experimental data and a mathematical model of these interactions was shown to describe dechlorination dynamics.

- An advanced solute transport model accounting for coupled flow and transport in fracture network and low-permeability matrix and reductive dechlorination, including donor consumption, has been developed. The developed numerical model has been applied to several field cases and provided a quantitative assessment of remediation time frames in clay till.

- The use of advanced models has shown that it is necessary to overcome mass transfer limitations in order to achieve remediation in reasonable timeframes. Therefore long remediation timeframes (>30-50 years) should be expected in clay tills. Furthermore it has been shown that the formation of more mobile daughter products during remediation might increase the risk to the groundwater. The modelling approaches have been employed for life cycle assessment of remedial options.

- An integrated approach combining chemical analysis and compound specific isotope analysis with reactive transport modelling was developed to identify and localize natural degradation processes in clay till. Abiotic and biotic degradation occurred in several zones inside the clay matrix.

5 FUTURE RESEARCH

A number of areas have been identified as needing further research in the area of risk assessment and bioremediation of chlorinated solvents in low-permeability media:

- **Development and "validation" of leaching models for risk assessment in fractured media.** Long term monitoring data are needed to identify the processes controlling the fate and transport of contaminant in low-permeability fractured media. More research should be done to test and evaluate the suitability of simple leaching models to assess short- and long-term risk to the groundwater.

- **Identification of factors controlling the development of bioactive zones in the clay matrix, and quantification of their influence.** Remediation timeframes are highly dependent on the establishment of reductive dechlorination inside the matrix. Factors controlling the distribution of bioactive zones are both physical (pore size distribution, porosity, presence of micro-fractures or larger geologic features), and biogeochemical (donor availability, carbon source, redox conditions). The capability to predict the development of bioactive zones at a particular site would allow the identification of where ERD is a suitable remediation technology.

- **Modelling the spreading of bacteria and donor in the clay matrix.** Upon identification of the processes controlling the development of bioactive zones, pore scale models should be developed to simulate and predict the spreading and growth of dechlorinating bacteria after injection in the subsurface. More research is also suggested for characterizing and modelling transport processes of bacteria in such systems, such as chemotaxis, or transport by electroosmosis.

- **Development of models of microbial communities involved in reductive dechlorination.** Reductive dechlorination is a complex process involving many interacting microbial communities, and models that take into account these interactions are needed, which could include individual-based modelling.

- **Identification and modelling of microbial processes controlling reductive dechlorination.** The recent advances in microbial techniques, with the possibility of quantifying gene products (mRNA, enzymes) and microbial activity, should be integrated in a modelling framework for improving prediction and quantification of reductive dechlorination, and other degradation processes. Genome-scale models, which can link genes to microbial growth kinetics, should be further developed and tested.

- **Development of practical tools for field applications.** In order to improve risk prediction and remediation design at field scale, practical tools should be developed, which are based on limited data, but include the relevant processes. Tools for engineering design, particularly models that can accurately predict donor consumption and on-going site maintenance needs, are needed. Such simple models should be tested and validated on field studies and/or by comparison with advanced numerical models.

- **Consideration of environmental impacts and economic evaluation of remediation technologies.** Decision-support tools for remedial choice should consider both environmental impacts (through life cycle assessment) and economic consideration. Incorporation of these factors in modelling of remediation alternative could for example help optimizing remediation design in order to reduce the costs and/or the global impacts of remediation activity.

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7 PAPERS

I. Chambon J.C., Binning, P.J., Jørgensen, P.R., and Bjerg, P.L., 2011. A risk assessment tool for contaminated sites in low-permeability fractured media. Journal of Contaminant Hydrology. 124 (1-4), 82-98.

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VI. Chambon, J.C., Damgaard, I., Jeannottat, S., Hunkeler, D., Broholm, M.M., Binning, P.J., and Bjerg, P.L., 2012. Identification and localization of degradation processes in clay till by combined analysis of chemical and isotope data with a numerical model. Manuscript.

The papers are not included in this web-version, but can be obtained from the library at DTU Environment.

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